OCT 24 1988

EPA 89/2:600/53-88/027

United States
Environmental Protection
Agency

Atmospheric Sciences
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S3-88/027 Sept. 1988

EPA

Project Summary

Theoretical Damage Function for the Effects of Acid Deposition on Galvanized Steel Structures

J. W. Spence and F. H. Haynie

A theoretical damage function for predicting the corrosion of galvanized steel structures by wet and dry deposition has been developed from thermodynamics and kinetics of atmospheric corrosion chemistry. The function mathematically expresses the competing reactions for the build up and dissolution of the basic zinc carbonate corrosion film with exposure time. Major findings as expressed by the theoretical function are as follows:

- **During periods of surface wetness, SO_2 reaching the surface reacts stoichiometrically with the zinc.**
- **Rain acidity reacts stoichiometrically with the zinc.**
- **The corrosion film of basic zinc carbonate is soluble in clean rain. The dissolution depends on the residence time of rain on the galvanized steel surface.**
- **Deposition velocity controls the rate of corrosion of galvanized steel structures by gaseous SO_2 during periods of wetness.**

Chamber and field exposures of galvanized steel were conducted to enhance the development of wet and dry deposition components of the theoretical damage function.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Atmospheric Sciences Research Laboratory (ASRL) within the Environmental Protection Agency is conducting an exposure research program on various materials of construction. A goal of this research is to develop damage functions for construction materials sensitive to wet and dry deposition. Wet deposition involves anthropogenic acidity within rain, snow, and fog, whereas gaseous pollutants are associated with dry deposition. A damage function is a mathematical expression that relates the rate of degradation of particular material to the environmental factors that contribute to the degradation.

Galvanized steel is one construction material that ASRL is investigating because it is widely used as roofing, siding, fencing, automotive bodies, etc., and is exposed to wet and dry deposition. Zinc is galvanically more active than iron and serves as an anode when the two metals are coupled, thereby protecting steel structures. The service life of galvanized steel structures depends on maintaining the zinc coating during exposure.

The use of an empirically-derived damage function from test panels to predict corrosion rates of galvanized steel products on real structures with environmental data of unknown accuracy and precision, raises considerable concern. Galvanized steel structures are not standard test specimens. Moreover it is not possible to determine the environmental parameters surrounding each structure with the same accuracy and precision as measured at test sites. It would produce not only biased errors, moreover

COMPLETED

the calculated confidence limits would be misleading.

To address this problem, the following steps are being taken to develop a damage function for galvanized steel that can be used to assess damage to real structures.

1. Use fundamental principles of thermodynamics and kinetics to derive a theoretical damage function.
2. Establish the applicability and consistency of the theoretical function using laboratory and field experiments.
3. Confirm applicability to changing real world environments using standardized exposure procedures at test sites where the accuracy and precision of environmental parameters are known, and
4. Check how well the function can predict corrosion rates on real structures with environmental parameters of unknown accuracy and precision.

This paper describes a damage function for galvanized steel structures that was developed using princples of thermodynamics and kinetics. The function which predicts the effects of wet and dry deposition is consistent with existing laboratory and field exposure data of galvanized steel and zinc specimens.

Theoretical Considerations

Galvanized steel exposed to the atmosphere soon forms a protective coating of basic zinc carbonate $2ZnCO_3 \cdot 3Zn(OH)_2$. Recent studies suggest that this coating consists of two layers, in which ZnO or $Zn(OH)_2$ is the adherent layer at the zinc surface, and the outer layer is basic zinc carbonate. The basic zinc carbonate film retards corrosion, and if its composition does not change or is not removed, corrosion would be parabolic with time. The film is soluble, however, in acidic solutions. Accordingly, it can be expected that (1) wet deposition will dissolve this protective film and (2) dry deposition, e.g., SO_2, will chemically change its composition into more soluble salts of zinc.

The net metal corroded (C) at any time can be accounted for as the sum of metal ion dissolved from the film (Bt_w) and the metal ion contained in the film (F).

$$C = F + Bt_w \qquad (1)$$

where C = corrosion (μm)
t_w = time of wetness (yrs)
B = solution rate of the protective corrosion film, a function of pollutant flux to the film (μm/yr)

The rate of corrosion film thickness growth in term of metal corroded is

$$\frac{dF}{dt_w} = A/F - B \qquad (2)$$

where A = function of diffusivity of corrosive species through film ($\mu m^2/yr$)

Diffusivity (A) may also be affected by pollutants. Integrating equation 2 under constant condition, Haynie derived the following transcendental equation:

$$C = Bt_w + A[1-\exp(-BC/A)]/B \qquad (3)$$

After long exposures, the term -BC/A is large and the term exp(-BC/A) approaches zero and equation 3 becomes a linear function:

$$C = Bt_w + A/B. \qquad (4)$$

i.e., when the long term steady state is reached, the rate of formation of the corrosion product film is equal to the rate of dissolution.

Corrosion should be controlled by the diffusion of ions through the corrosion product film, a function of diffusivity and film thickness. Dissolution removal of the film will increase the corrosion rate. When exposed in a polluted environment, the corrosion product film would be thin hence linear corrosion would occur early in the exposure. In a nonpolluted environment, the film would continue to grow and curvature of the corrosion-time curve would be observed. The corrosion function becomes linear with respect to the solubility term (Bt_w and the amount of corrosion in the insoluble film (F=A/B) remains constant with respect to a given set of solubility conditions (B). The solubility term (Bt_w) can be separated into environmental components involving wet and dry deposition. These wet and dry delivery mechanisms serve as a convenient means of describing the corrosion rate-controlling factors. We attempt to express corrosion as a sum of contributions from wet and dry deposition.

Wet Deposition

Rain contributes not only to the time of wetness but also delivers reactive species (SO_4^{-2}, H^+, HCO_3^-, etc.) to the surface. The rate of delivery is the amount of rain per unit time multiplied by the ion concentration.

Acid Reaction with Metal

The acidity in rain, pH or (H^+), can increase the corrosion rate by increasing the solubility of the corrosion product film. These ions also are consumed and replaced electrochemically in solution by zinc ions, $2H^+ = Zn^{++}$. The reaction is probably fast enough so that the rain residence time on the surface is not a factor. The upper limit of acid zinc corrosion simply is a function of the amount of rainfall and its pH. Hydrogen ion concentration [H^+], equivalents per liter, is 10^{-pH}. Hence, hydrogen ion equivalents delivered per cm^2 of horizontal surface is the amount of rain (R), cm, times 10^{-3-pH}. One equivalent of H^+ per cm^2 of zinc will consume 4.6 cm of zinc (the ratio of equivalent weight to density). Thus zinc corrosion caused by rain acidity is

$$C_{ra} = 46\ R10^{-pH} \qquad (5)$$

where R = total rainfall during exposure (cm)
C_{ra} = corrosion due to acidic rain (μm)

With rain assumed to fall vertically, the average loss on both sides of a specimen exposed at 30° from the horizontal will be less by a factor of 0.5 cos 30°.

Dissolution of Zinc Carbonate

Clean rain solubility is associated with acidity caused by dissolved carbon dioxide from the atmosphere. This produces the HCO_3^- ion that contributes to the solubility of the basic zinc carbonate. The solubility of zinc carbonate varies with the concentration of CO_2 in aqueous solutions which depends on the atmospheric concentration of CO_2 and temperature; as temperature increases, the solubility decreases. If it is assumed that rain water equilibrates with both atmospheric CO_2 and the galvanized steel surface, then "clean rain" corrosion can be calculated from the solubility of zinc carbonate.

The solubility of a metal carbonate ($MeCO_3$) in water containing dissolved carbon dioxide can be treated as an equilibrium problem between two condensed phases and a reactive gas. The enthalpy, entropy and heat capacity are used to calculate the equilibrium constants for the relationship.

$$K = 4(Me^{+2})^3 p_{CO_2}, \text{ or} \qquad (6)$$
$$ME^{+2} = [KP_{CO_2}/4]^{1/3}$$

and expressed as a function of temperature using appropriate thermodynamic data for zinc.

$$K = \exp[-1266 + 9583/T + 1359\ln T] \qquad (7)$$

When the mean value for atmospheric concentration of carbon dioxide of approximately 345 ppm, or 0.000345 atmospheres pressure as reported in Chemical & Engineering News is substituted above, the equilibrium concentration of zinc ion dissolved from zinc carbonate by air-saturated water is $4.42 \times 10^{-2} K^{1/3}$ moles/liter. Thus R cm of rain will dissolve $4.42 \times 10^{-4} RK^{1/3}$ moles of zinc carbonate. If it is assumed that each mole of zinc carbonate is replaced by corrosion of an equivalent amount of zinc metal, then, multiplying by the ratio of zinc atomic weight to density gives the amount of corrosion by "clean" rain (C_{rc}) as

$$C_{rc} = 4.05\ rRK^{1/3} \quad (8)$$

where a residence time factor (r) has been included to allow for the fact that rainwater may not remain in contact with the surface long enough to reach equilibrium.

Dry Deposition

Both gaseous and particulate pollutants are deposited to surfaces, but the deposition mechanism differs. The rate of delivery of gases to a surface is determined by air flow, whereas particulate matter is deposited by gravitational settlement and wind-blown impaction.

Deposition Gases

The ambient concentration of a gaseous pollutant is related to pollutant flux to a surface by defining deposition velocity (V_d) as the ratio of the flux to the ambient concentration measured at some point away from the surface. From analogy with momentum transport, gases with a Schmidt number of approximately one that readily absorb on a surface have a deposition velocity of:

$$V_d = V^{*2}/V = Vf/2 \quad (9)$$

where V^* = friction velocity,
V = average windspeed near the surface, but not within the boundary layer.

The friction velocity (V^*) is equal to $V\sqrt{f/2}$ where f is the friction factor. From boundary layer theory for smooth flat plates, the equation for the friction factor is:

$$f = 0.03/(RE_L)^{1/7} \quad (10)$$

where RE_L = Length Reynolds number, LV/ν,
L = length of surface over which air flows, and
ν = kinematic viscosity of air (0.15 cm^2/s at 20°C).

Similarly for air flowing perpendicular to cylinders, such as fencing, where diameter replaces length in the Reynolds number the friction factor is:

$$f = 0.6/(RE)^{1/2} \quad (11)$$

Another factor to consider is that windspeeds are normally measured at the top of a tower while corrosion panels as well as fencing and siding are usually closer to the ground. Windspeed varies with height from the ground and can be approximated by the following relationship:

$$V^+ = 8.5 + 2.5\ \ln(Z/e) \quad (12)$$

where V^+ = a dimensionless velocity (V/V^*),
V^* = friction velocity for the ground surface velocity profile,
Z_1 = the measured height above ground, and
e = the surface roughness height.

The ratio of the velocity at exposure height (Z_2) to the velocity at measured height (Z_1) with a surface roughness of 0.1 m will be $[1 + 0.175\ln(Z_2)]/[1 + 0.175\ln(Z_1)]$.

From the above relationships it can be seen that wind velocity, and shape and size of a surface affect deposition velocity. It is informative to compare deposition velocities calculated for 10.2 x 15.2 cm^2 corrosion specimens, with those for a three meter length of sheet and nine gauge (3.76mm diameter) galvanized fence wire. With deposition velocity (V_d) in cm/sec and windspeed (V) in m/sec, the results are:

Corrosion Specimen: $V_d = 0.414V^{6/7}$ (13a)

Large Sheet: $V_d = 0.259V^{6/7}$ (13b)

Fencing: $V_d = 1.89V^{1/2}$ (13c)

For an average windspeed at the surface of 3 m/s, the respective deposition velocities are 1.06 cm/s, 0.66 cm/s, and 3.27 cm/s. Thus, fencing is expected to corrode faster than roofing and siding when exposed to the same gaseous pollutants.

While gases may be delivered to the surface at calculated deposition velocities, the net flux of a gas is not necessarily proportional to the deposition velocity. For example, sulfur dioxide is readily absorbed and then reacts with a wet zinc surface whereas nitrogen dioxide does not. A dry zinc surface is soon saturated with a monolayer of sulfur dioxide, hence the net flux is zero, i.e., the amount delivered is equal to that removed. This monolayer can be consumed later when the surface becomes wet. A monolayer of SO_2 is equivalent to 1.29 x 10^{-4} micrometers loss of a clean zinc surface. Unless the SO_2 concentration is extremely low a monolayer will form between periods of wetness (usually daily).

Sulfur dioxide, which has a solubility of 1.24 mole/latm in liquid water at 25°C, not only readily dissolves in water but also reacts with zinc. Therefore when a zinc surface is wet, the rate of reaction of SO_2 will be controlled by the calculated deposition velocity.

A metal surface will be wet by rain or dew. The presence of hygroscopic salts, e.g., $ZnSO_4$, increases the effective dew point, or equivalently lowers the critical relative humidity as:

$$RH_c = 96.3 - 0.313DP \quad (14a)$$

where DP = ambient dew point (C°)

Therefore, time-of-wetness (tw) can be defined as the amount of time that it is raining plus when the relative humidity exceeds 96.3 - 0.313DP and the dew point is greater than 0°C (not freezing). A relationship for relative humidity as a function of temperature (T) and dew point (DP) above °C is

$$RH = 100 \exp[-.07222 + 0.00025(T + DP)(T-DP)] \quad (14b)$$

where T and DP = temperature and dew point, °C respectively

The total zinc corrosion (C_d) due to deposition of gaseous sulfur dioxide during periods of surface dryness (C_m) and wetness can be calculated as follows:

$$C_d = C_m + 0.045\ V_d(SO_2)t_w \quad (15)$$

where $C_m = 1.29 \cdot 10^{-4} A_r N$
A_r = actual to apparent surface area ratio,
N = number of dryness periods, and
V_d = deposition velocity (cm/s).

During a year with daily periods of dryness and A_r equals two, the corrosion due to the monolayer(C_m) of SO_2 equals 0.094 micrometers for a year. This contribution should not be very significant unless SO_2 concentrations during period of wetness are relatively low.

Theoretical Damage Function

Combining all of the theoretical components contributing to the corrosion of zinc and galvanized steel the following damage function is obtained:

$$C = F + C_{ra} + C_{rc} + C_d, \text{ or} \quad (16)$$
$$C = F + 46R10^{-pH} + 3.9rRK^{1/3} + 1.29.10^{-4}A_rN + 0.045V_d(SO_2)t_w$$

For this function, F represents the zinc corrosion remaining in the corrosion film, the components $C_{ra} + C_{rc}$ represent the effects of acidic rain and clean rain for wet deposition, and the last two components represent the effect of dry deposition of gaseous SO_2 that occurs during periods of surface dryness and wetness.

A listing of all the terms, the appropriate units, and definition of these terms for the components of the theoretical damage function is shown in Table 1. There are twenty-two terms not counting temperature, dewpoint, length and diameter.

Experimental Procedure

Laboratory and field exposure experiments were conducted to enhance the development of the theoretical damage function. The galvanized steel panels for these experiments were prepared from sheet stock of 20-gauge zinc-coated (hot-dipped) steel. The average thickness of the coating was 20 μm. The panels were cleaned prior to exposure by two minute immersion in 10% aqueous solution of ammonium chloride (NH_4Cl) at 60 to 80°C. The panels then were rinsed with deionized water, anhydrous methanol, and then air dried.

Laboratory Exposures

An exposure system consisting of two flow chambers coupled in parallel to an 11.3 cm^3 smog chamber (Figure 1) was used to conduct the laboratory studies. A complete description of the exposure system, experimental procedures, and results has been previously reported.

Field Exposures

Galvanized steel and other metals are being exposed at five field sites where environmental measurements are continuously recorded. At the North Carolina material exposure sites, a study to partition the effects of rain and no rain on galvanized steel panels was conducted from 1982 to 1984. In this study two sets of galvanized steel panels were exposed using an automatic covering device that covered one set of panels during each rain event.

In order to study the effects of rain acidity (pH) as well as dry deposition of gases on the corrosion of galvanized steel, another automatic covering device (Figure 2) that sprays a set of panels during each rain event was installed at the North Carolina materials exposure site. Three sets of galvanized steel panels were exposed. Two of them were moved under the cover during each rain event. One of the covered sets was sprayed with approximately the same volume of deionized water(5.6 pH) as measured for each rain event. The other set is not sprayed. The third set of panels remained exposed to ambient dry and wet acidic deposition. Following the rain event, the two covered sets of panels were moved to the boldly exposed condition. Plastic bottles (Figure 2) are used to collect rain and spray runoff from the skyward surfaces of the panels. The runoff experiments were initiated in 1985 at the North Carolina materials exposure site.

Discussion

Results of laboratory and field experiments were used to determine the applicability and consistency of the theoretical damage function. In these experiments, chemical species that were identified in runoff collections represent the soluble corrosion products that form due to wet and dry deposition. Characterization of the corrosion surface film that forms on galvanized steel panels during ambient exposures was not investigated in these experiments but is being conducted by the Bureau of Mines.

Table 1. *Definition of terms for the theoretical damage function*

Terms	Units	Definition of Terms
C	μm	Total zinc corrosion
C_{ra}	μm	Corrosion caused by rain acidity = $46R \times 10^{-pH}$
C_{rc}	μm	Clean rain effect = $3.9rRK^{1/3}$
C_m	μm	SO_2 monolayer absorption effect = $1.29 \times 10^{-4}A_rN$
V_d	cm/s	Deposition velocity = $V^2/V = Vf/2$
SO_2	μg/m³	Sulfur Dioxide concentration
t_w	years	Time-of-wetness = when raining plus when critical relative humidity (RH_c) is exceeded and dew point (DP) exceeds 0°C
F	μm	Zinc loss remaining in film = $A[1-\exp(-BC/A)]/B$
R	cm	Rainfall
pH	pH units	a measure of acidity
K		equilibrium constant $K^{1/3} = \exp[-42/2 + 3494/DP + 4.53\ln(DP)]$
r		Rain residence time factor = < 1
A_r		Ratio of actual to apparent surface area
N		Number of periods between wetness events
V^*	cm/s	Friction velocity = $V\sqrt{f/2}$
V	cm/s	Windspeed approaching surface
RH_c	%	Critical relative humidity = 96.3 - 0.313 DP for zinc sulfate, or 75% with large amounts of NaCl
A	μm²/year	Film diffusivity coefficient
B	μm/year	Dissolution coefficient = $(C_{ra} + C_{rc} + C_m + 0.045\ V_dSO_2tw)/tw$
f		Friction factor = $0.03/(RE_L)^{1/7}$ for smooth plates = $0.6/(RE)^{1/2}$ for cylinders
RE		Reynolds Number = LV/ν for plates, L = length (cm), ν = Kinematic viscosity of air (0.15 cm²/s at 20°C)

BEST COPY AVAILABLE

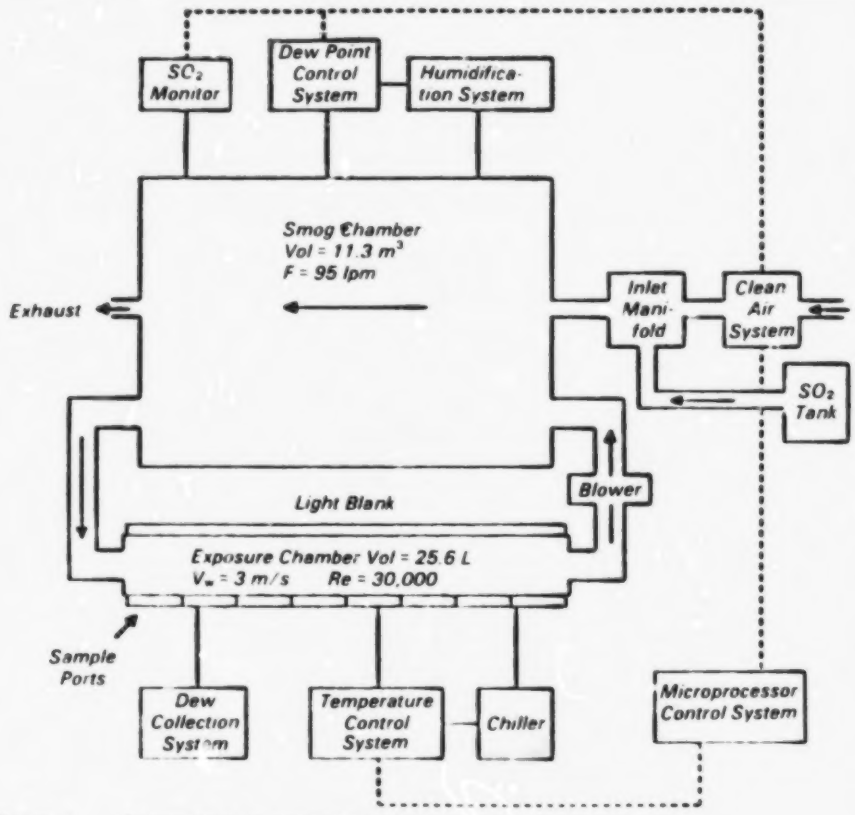

Figure 1. Schematic of flow chamber system.

Wet Deposition Component

The wet deposition component of the theoretical function has terms for both anthropogenic rain acidity (C_{ra}) and clean rain (C_{rc}). Controlled field studies were conducted at the rural North Carolina site to investigate the effect of rain on diffusivity (A) and solubility (B) of the corrosion product film, equation 3. Rain was found to have an effect on both dissolution and diffusivity processes. Rainfall almost doubled the diffusivity of species through the corrosion product film, whereas the solubility of $ZnCO_3$ in rain explained most of the variability associated with the solubility (B). The clean rain term, C_{rc}, involves the solubility of zinc carbonate within the corrosion product film. The solubility is a function of the CO_2 that is dissolved and dissociated in water. A relationship for the zinc carbonate equilibrium constant, equation 7, was developed in terms of dew point temperature. The equilibrium constant can be used to calculate the maximum clean rain effect. The residence time of incident rain on small specimens exposed at 30° from the horizontal is not long enough for equilibrium to be obtained. The residence time varies with rain intensity and should be proportional to the length of surface over which the rain flows and the angle of exposure. This suggests that equilibrium of the zinc carbonate solubility may be reached for large sheets such as roofing. On the other hand, it may be more appropriate to assume that clean rain has little effect on fence wire.

In other controlled field exposures at the North Carolina site, the analysis of runoff collections from exposed galvanized steel panels indicated that 99% of the incident hydrogen ion within the rain was consumed. The zinc coating as well as the corrosion product film are strong buffers of incident hydrogen ion. Therefore, the contribution for rain acidity (C_{ra}) for the theoretical damage function has no residence time factor. The hydrogen ions within rain will likely be consumed by large galvanized sheets such as roofing as well as by fence wire.

Dry Deposition Component

Corrosion studies of galvanized steel panels that were conducted in this program confirm not only the importance of SO_2 during periods of surface wetness but also the accumulation of SO_2 during periods of surface dryness. Therefore, the dry deposition component (C_d) of the theoretical damage function has terms for the accumulation of SO_2 during periods of surface wetness and during periods of surface dryness.

Sulfur dioxide will deposit on a dry surface of galvanized steel to form a saturated monolayer of SO_2. The contribution of the SO_2 monolayer to corrosion of galvanized steel structures (C_m) is a function of the exposed surface area and the number of dryness periods. The value of $1.20 \cdot 10^{-4}$ for the coefficient represents the reaction of the monolayer of SO_2 with zinc. This effect was observed in chamber studies, however it likely occurs during ambient exposures of galvanized steel structures.

The last term of the dry deposition component, $0.045V_d(SO_2)t_w$, represents the corrosion due to the deposition of SO_2 during periods of surface wetness of galvanized steel structures. Deposition velocity (V_d) which determines gaseous flux to a surface from concentration measurements was incorporated into this term of the theoretical damage function. Deposition velocity is determined from windspeed data and differs according to the shape and size of the galvanized steel structure. For a given windspeed, deposition velocity for fence wiring is higher than for sheet roof or siding. Therefore fence wiring is expected to corrode faster than sheet products when exposed to the same ambient levels of pollutant gases.

The coefficient, 0.045, that appears in this term of the dry deposition component is the stoichiometric coefficient for the reaction of SO_2 with zinc to form zinc sulfate. This result is consistent with the linear damage function that was developed for the corrosion of galvanized steel in St. Louis.

Chamber studies have confirmed time of wetness (t_w) as an essential term of the dry deposition component of the theoretical damage function. Ambient concentrations of SO_2 should be accumulated during periods of surface wetness of galvanized steel structures. As previously defined, time of wetness (t_w) is the amount of time that it is raining plus when the relative humidity exceeds a critical relative humidity and when the dew point is greater than 0°C (not freezing). The critical relative humidity and relative humidity can be calculated from equations 14a and 14b, respectively. These

BEST COPY AVAILABLE

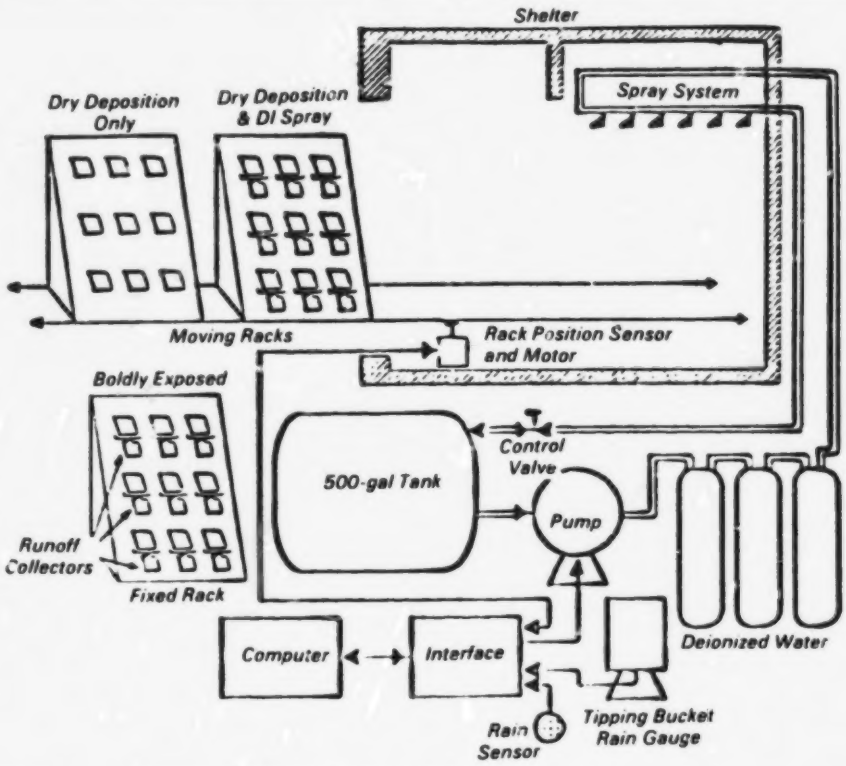

Figure 2. Schematic of automatic covering device.

equations require temperature and dew point to be available.

Conclusions

A theoretical damage function for predicting the corrosion of galvanized steel structures by wet and dry deposition has been developed from thermodynamics and kinetics of atmospheric corrosion chemistry. The function mathematically expresses the competing reactions for the build up and dissolution of the basic zinc carbonate corrosion film with exposure time. Major findings as expressed by the theoretical function are as follows:

- During periods of surface wetness, SO_2 reaching the surface reacts stoichiometrically with the zinc.
- Rain acidity reacts stoichiometrically with the zinc.
- The corrosion film of basic zinc carbonate is soluble in clean rain. The dissolution depends on the residence time of rain on the galvanized steel surface.
- Deposition velocity controls the rate of corrosion of galvanized steel structures by gaseous SO_2 during periods of wetness.

The EPA authors J. W. Spence and F. H. Haynie are with the Atmospheric Sciences Research Laboratory, Research Triangle Park, NC 27711.
The complete report, entitled "Theoretical Damage Function for the Effects of Acid Deposition on Galvanized Steel Structures," (Order No. PB 88-234 059/AS; Cost: $14.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA authors can be contacted at:

Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

BEST COPY AVAILABLE

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/600/S3-88/027